

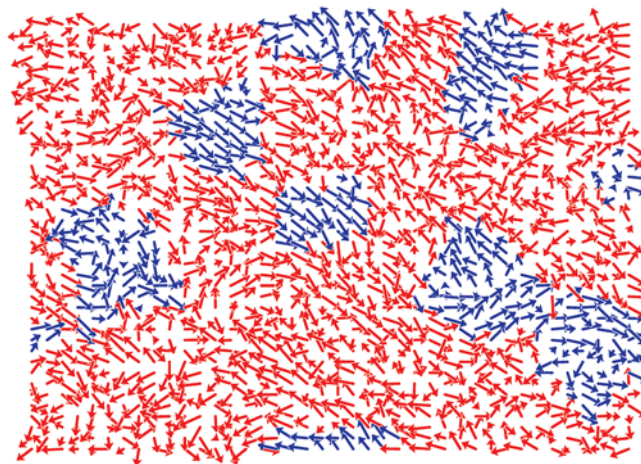
## Theory and Modeling of Electronic Materials

*Optimizing the properties of electronic materials requires fundamental understanding of the origin of their useful properties and computational tools that connect atomic-scale knowledge obtained from first-principles calculations to properties that emerge at larger length scales. We are developing first-principles based modeling tools for calculating the physical properties of materials as a function of chemical ordering on different length scales and how these properties respond to changes in the environment (temperature, pressure, electric field, etc.). Such techniques have applications in a variety of areas, including dielectrics, dilute spin glass magnets, light-emitting diodes, multiferroics, phase diagrams, piezoelectrics, semiconductors, and spectroscopy.*

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Understanding and predicting the physical properties of solid solutions is a difficult problem in general. Even in the simplest case of a harmonic crystal, the vibrational energy as a function of atomic arrangement can have a strong affect on the phase diagram. The calculated maximum temperature for the miscibility gap in NaCl-KCl is reduced by about 50 % when vibrational entropy is included, and the agreement with the experimental phase diagram is much improved. Many systems with useful electromechanical properties, such as  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN), the relaxor ferroelectric that is a constituent of the ultrahigh piezoelectric compound PMN-PbTiO<sub>3</sub>, are highly anharmonic. Effective Hamiltonian ( $H_{\text{eff}}$ ) techniques have been developed to simplify the modeling of these systems, but the effect of chemical disorder on the lattice dynamics of solid solutions is not well understood. We published a methodology, based on maximum localization, for automatically determining the appropriate  $H_{\text{eff}}$  basis for solid solutions and showed that it correctly reproduces the phonon density of states for low-frequency phonons. In PMN, these phonons were determined to be of two types: those involving displacements of Pb, and those involving rotations of oxygen octahedra.

Experiments suggest that the relaxor behavior in  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (PSN) is associated with nanoscale chemically ordered regions in a disordered matrix. We performed a molecular dynamics simulation of a PSN  $H_{\text{eff}}$  on a 320000 atom cell. Polarization fluctuations are much larger in the chemically ordered regions,



**Figure 1:** Snapshot of local polarization in PSN model showing larger polarization and polarization correlations in the chemically ordered regions (blue) than in the disordered matrix (red).

which thus dominate the dielectric behavior of PSN near its dielectric peak. This work demonstrates the importance of  $H_{\text{eff}}$  methods that allow us to make a detailed investigation of the effects of nanoscale chemical ordering on dielectric properties.

The semiconductor industry is interested in  $\text{HfO}_2$  as an alternate gate dielectric material. Experiments typically show significant numbers of defects in  $\text{HfO}_2$ . First principles calculations show that O vacancies are most stable on the 4-fold coordinated O site and that  $\text{HfO}_2$  remains insulating with both a neutral and a 2+ charged vacancy. Work is underway to determine how each kind of vacancy affects the dielectric properties.

Quantitative modeling of mechanical behavior at the nanoscale requires connecting the large-scale elastic displacement fields experienced by the whole device to the small-scale atomistic regions where bond breaking can mark the initiation of device failure through fracture or plastic deformation. We are working to develop multiscale models for connecting the microscopic applied load in a nanoindentation experiment to the initiation of the first broken bond. The sample is a bulk Al single crystal with a  $\langle 111 \rangle$  surface.

### Contributors and Collaborators

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